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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

11 June 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2001-136**  
Phillips, Shawn; Haddad, T.S., Blanski, R.L., "Molecularly Reinforced Polymers" (VuGraphs)

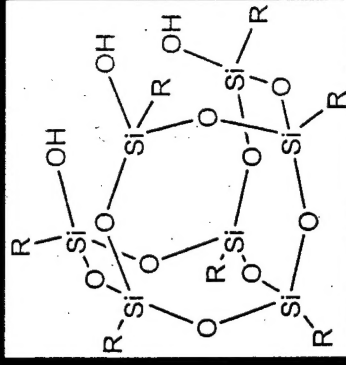
**2001 International Symposium on Nanocomposites**  
**(Chicago, IL 25-27 June 2001)(Deadline: 24 June 2001)**

**(Statement A)**

# *POSS Nanostructured Chemicals: Past & Present*



**Dr. Shawn H. Phillips**  
Polymer Working Group  
Air Force Research Lab, Edwards



DISTRIBUTION STATEMENT A:  
Approved for Public Release -  
Distribution Unlimited

Dr. Tim Haddad, Dr. Rusty Blanski, Dr. Brent Viers, Capt. Rene Gonzalez, Maj Steve Svejda, Mr. Brian Moore, Mr. Justin Leland, Mr. Pat Ruth, Dr. Kevin Chaffee, Mr. Hieu Nguyen, Mr. Paul Jones

# Edwards AFRL

Modesto

San Jose

Salinas

Fresno

Bakersfield



Los Angeles

Ontario

Orange

Oceanside

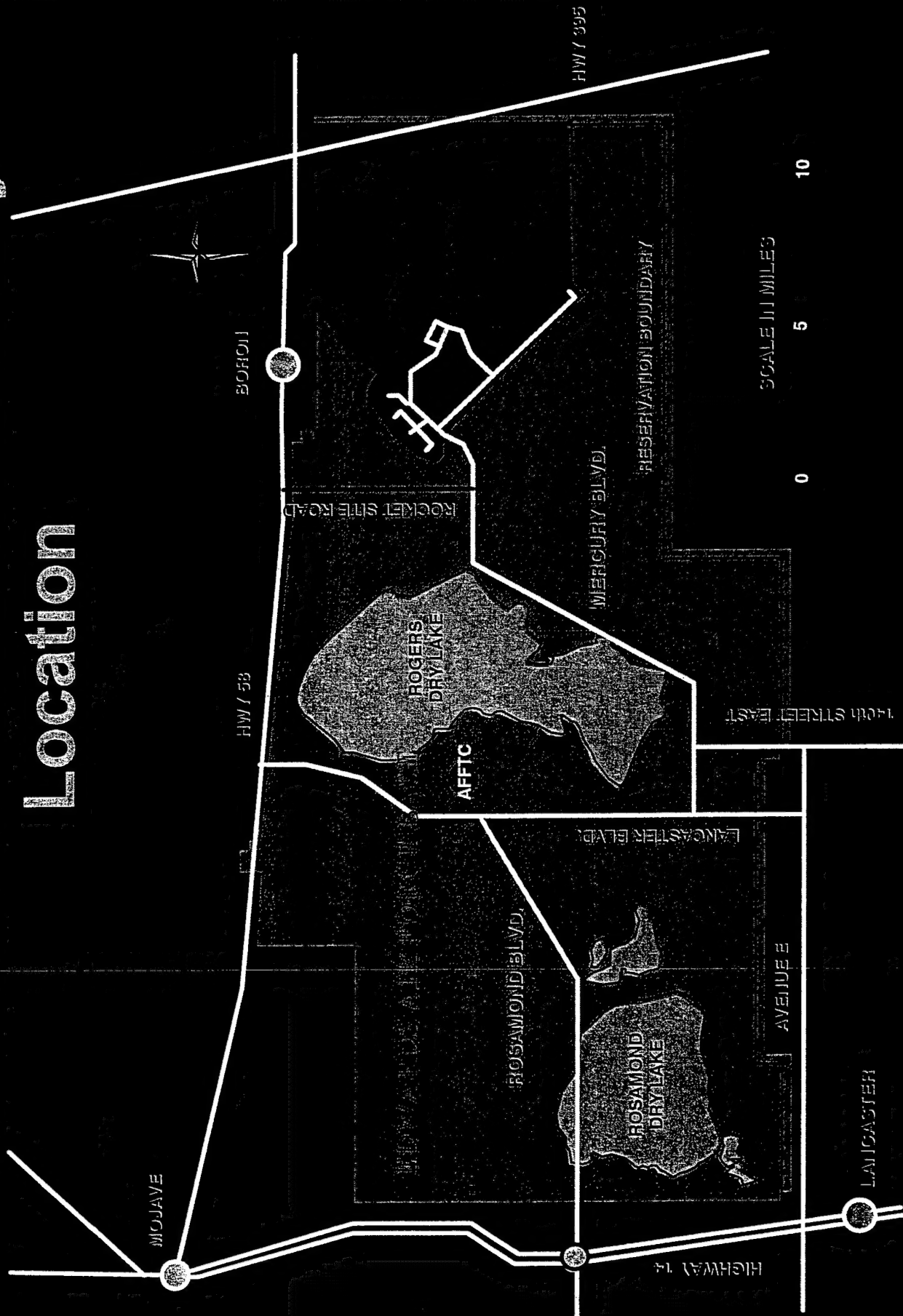
San Diego

Phoenix

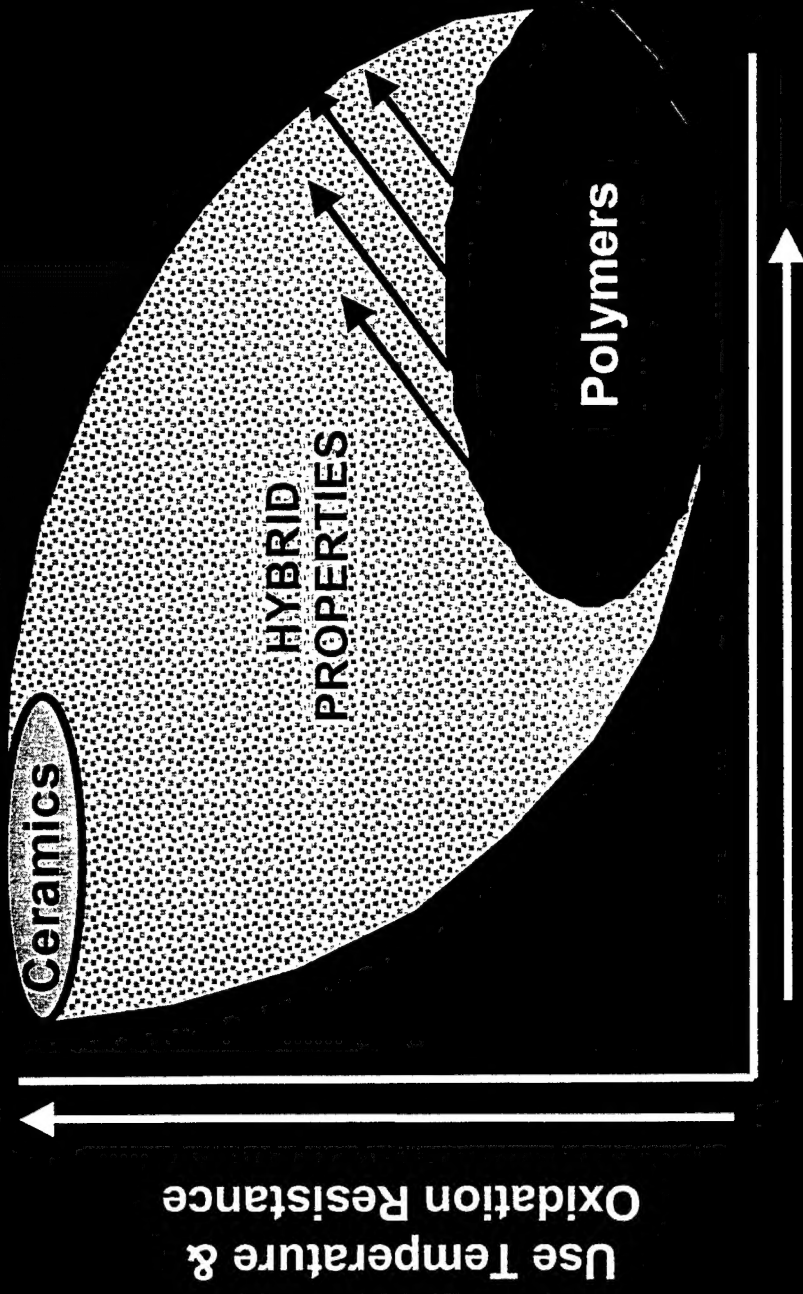
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# Air Force Research Laboratory Location



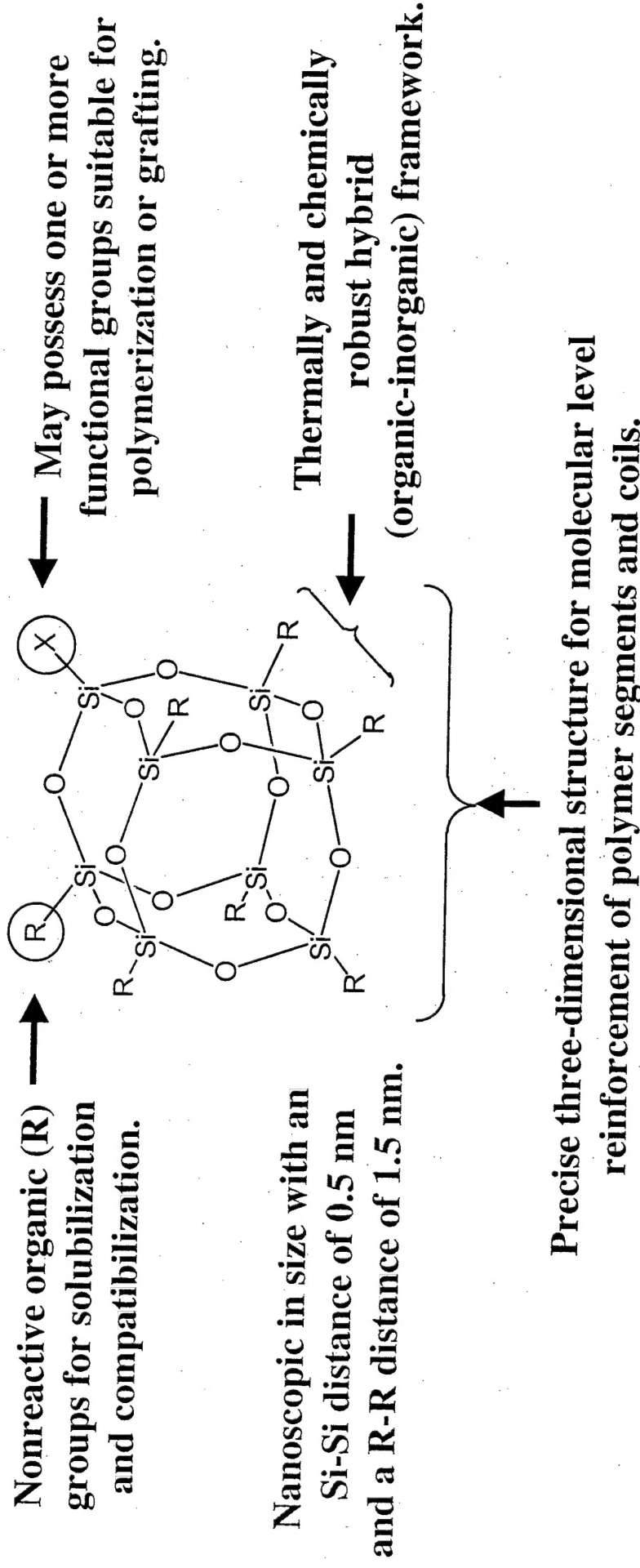
# Multiple Applications/Multi-Function



- Improve High Performance Polymers/ Transform Commodity Polymers into High performance Polymers
- Develop Multi-Functional Materials/ Replace Metal Parts with Polymers

# Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS) Molecule

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The maximization of property enhancements in polymers results from interaction at the nano-level (Edwards AFRL/PRSM ---> POSS monomers)

# Physical Aspects

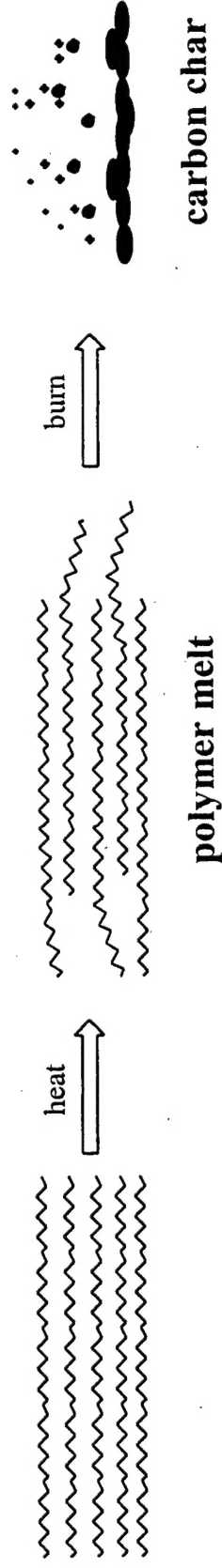
Particle Type	Particle Diameter
polymer segments	5 - 50 Å
C60 "buckyball"	7 Å
Cy <sub>8</sub> T <sub>8</sub> POSS	15 Å
silicate layer	10-100 Å
random polym. coils	50 - 100 Å
colloidal silica	90 - 800 Å
max. extended lengths	80 - 90,000 Å
crystalline lamellae	10 - 90,000 Å
fillers / atmospheric dust	20 - 1,000,000 Å

H	He
Li	Ne
Be	F
B	O
C	N
N	Ar
O	Cl
F	S
Ne	P
Na	Ca
Mg	K
Al	Br
Si	I
P	Xe
S	Rn
Cl	
Ar	
K	
Ca	
Sc	
Ti	
V	
Cr	
Mn	
Fe	
Co	
Ni	
Cu	
Zn	
Ga	
Ge	
As	
Se	
Br	
Kr	
Rb	
Sr	
Y	
Zr	
Nb	
Mo	
Tc	
Ru	
Rh	
Pd	
Ag	
Cd	
In	
Sn	
Pb	
Bi	
Po	
At	
Rn	
Fr	
Cs	
Ba	
Ra	
La	
Ce	
Pr	
Nd	
Pm	
Sm	
Eu	
Gd	
Tb	
Dy	
Ho	
Er	
Tm	
Yb	
Lu	
Ac	
Th	
Pa	
U	
Np	
Pu	
Am	
Cm	
Bk	
Cf	
Es	
Fm	
Md	
No	
Lr	

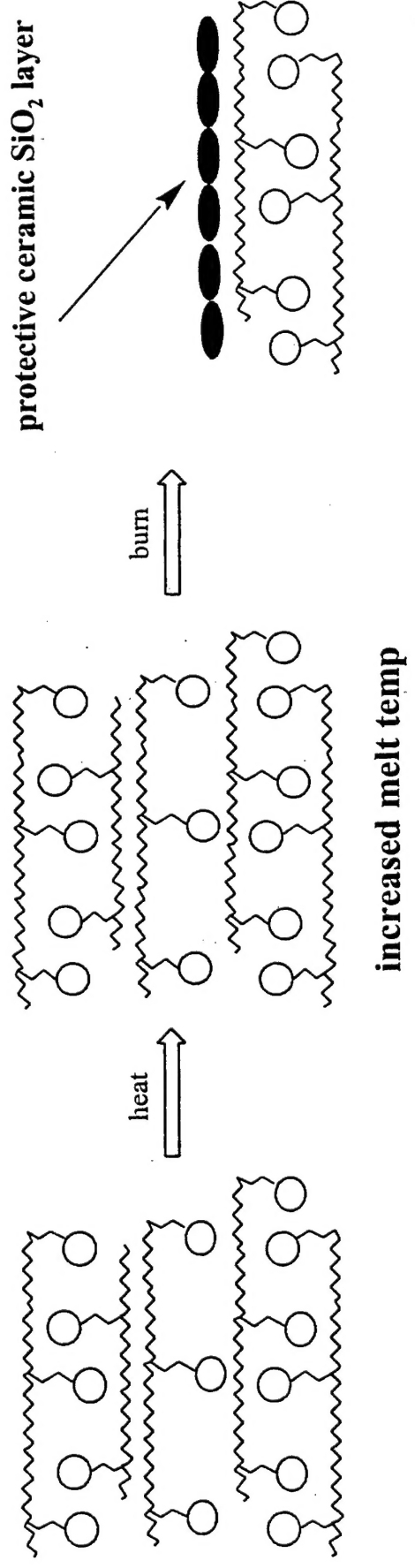
# Chemical Composition

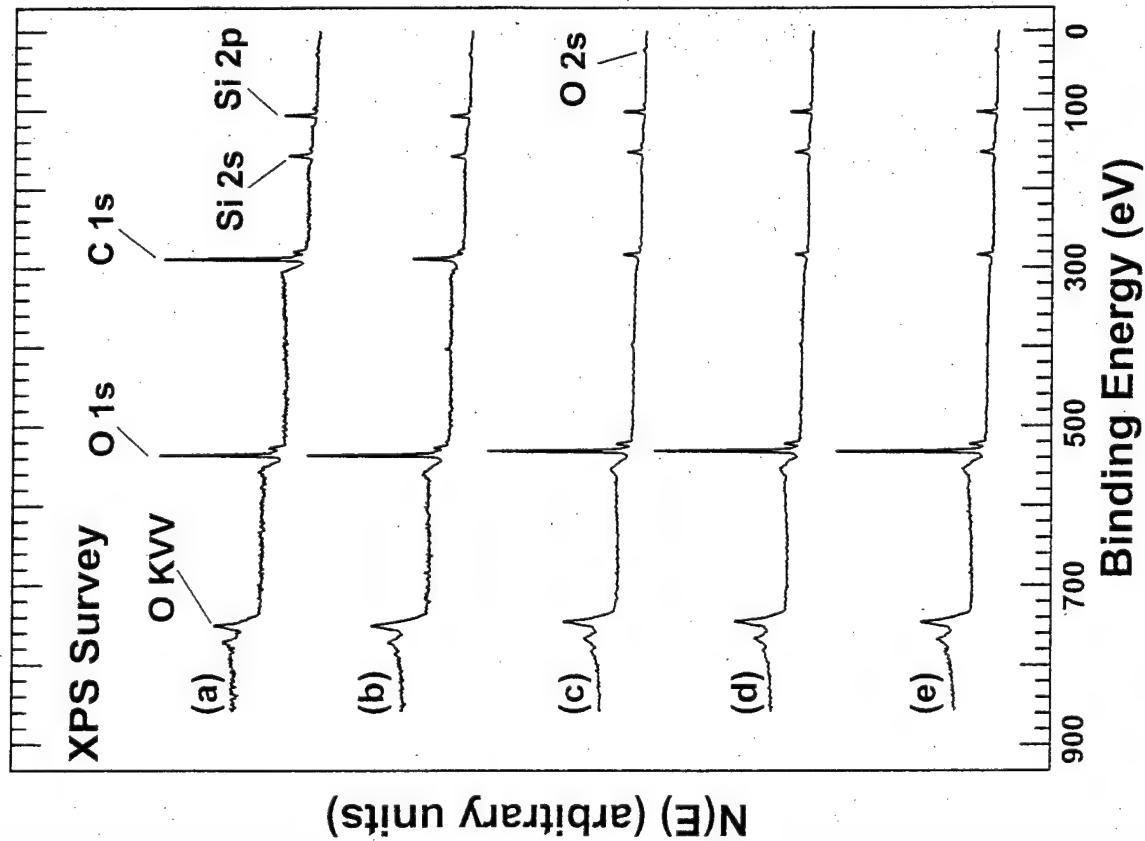
# *POSS for Flame Retardant Materials*

## Traditional Polymer

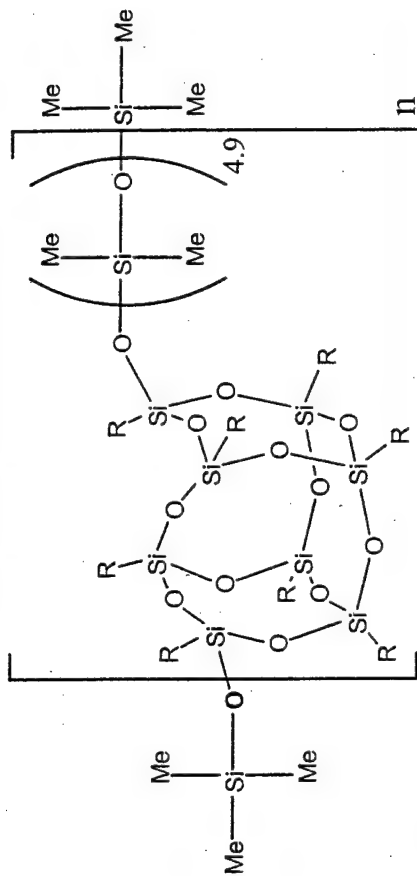


## POSS Polymer



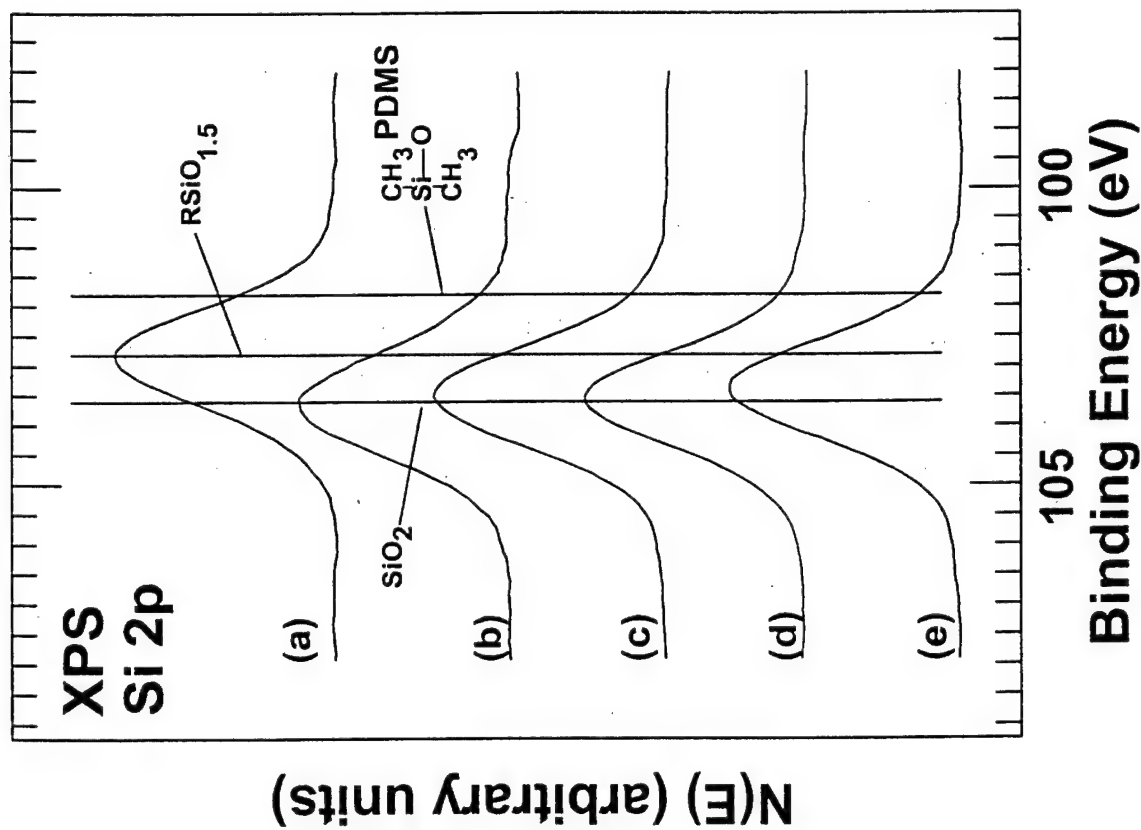


## POSS Siloxane



Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

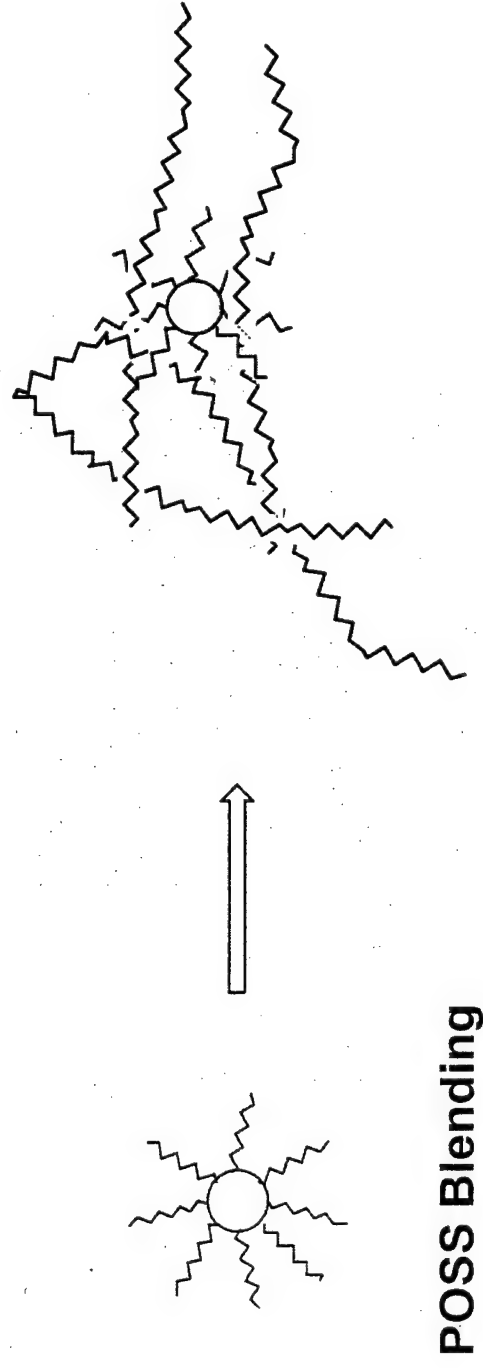
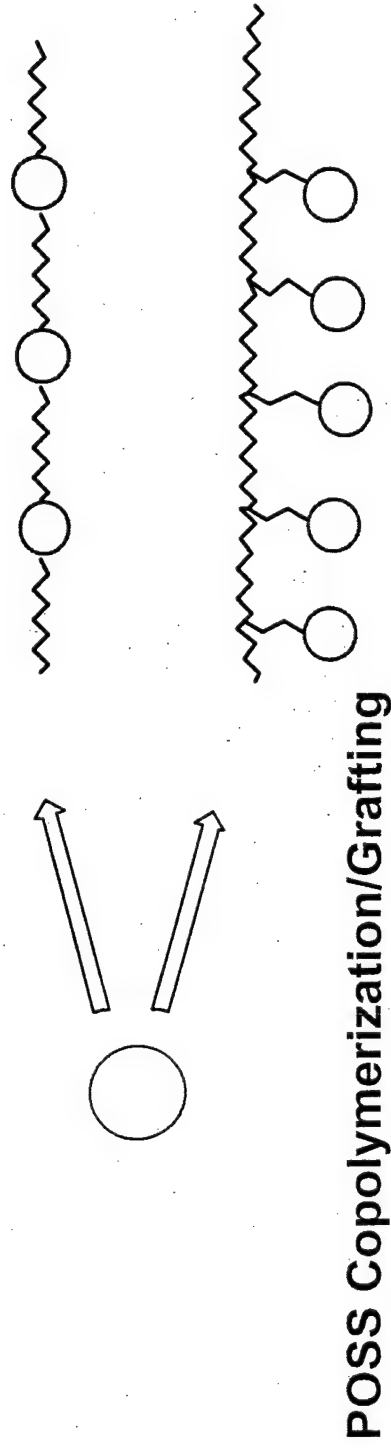
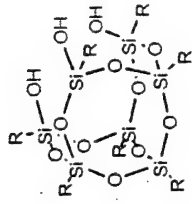
XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.



High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

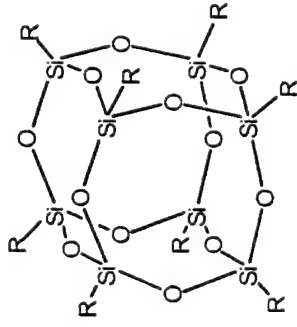


# POSS Polymer Incorporation

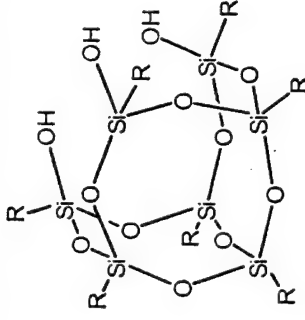


**Size & Shape**

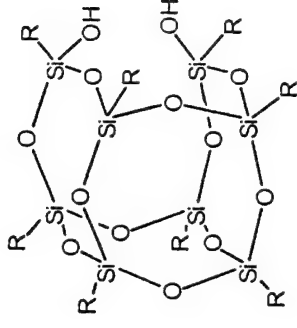
# POSS Diversity



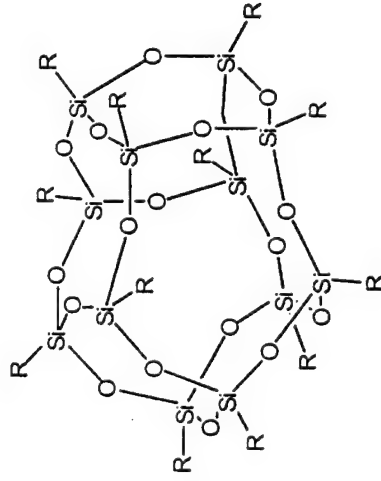
**R = Methyl**  
**Isobutyl**  
**Cyclopentyl**  
**Cyclohexyl**  
**Isooctyl**  
**Phenyl**  
**Phenethyl**  
**Octadecene**



**R = Isobutyl**  
**Cyclopentyl**  
**Cyclohexyl**  
**Isooctyl**  
**Ethyl**



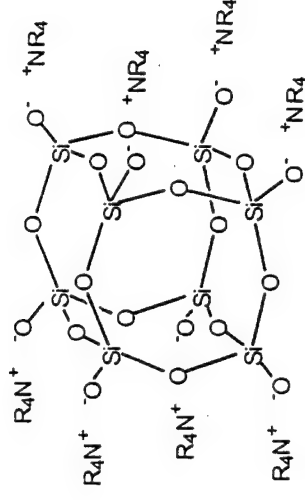
**R = Isobutyl**  
**Cyclopentyl**  
**Cyclohexyl**  
**Isooctyl**



**R = Phenyl**  
**Trifluoromethylpropyl**

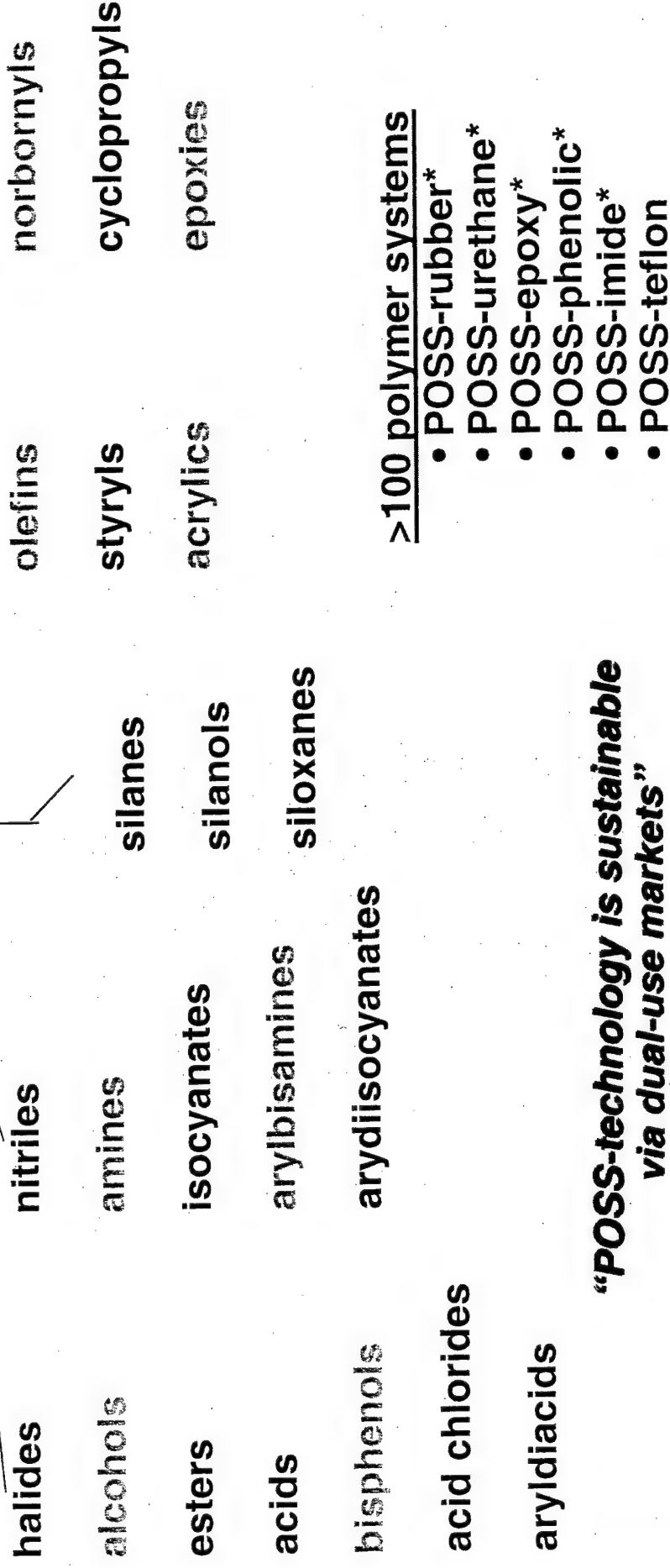
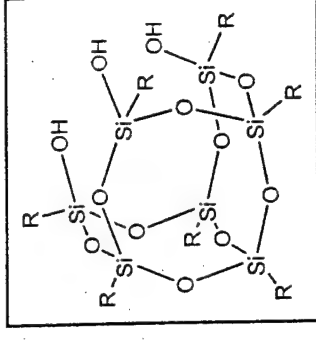
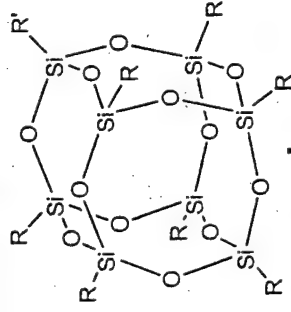
**Polydisperse Cages**  
**(T<sub>8</sub>, T<sub>10</sub>, T<sub>12</sub>)**

**R = Vinyl**  
**Phenethyl**



**R = Methyl**

# POSS Monomer/Polymer Trees



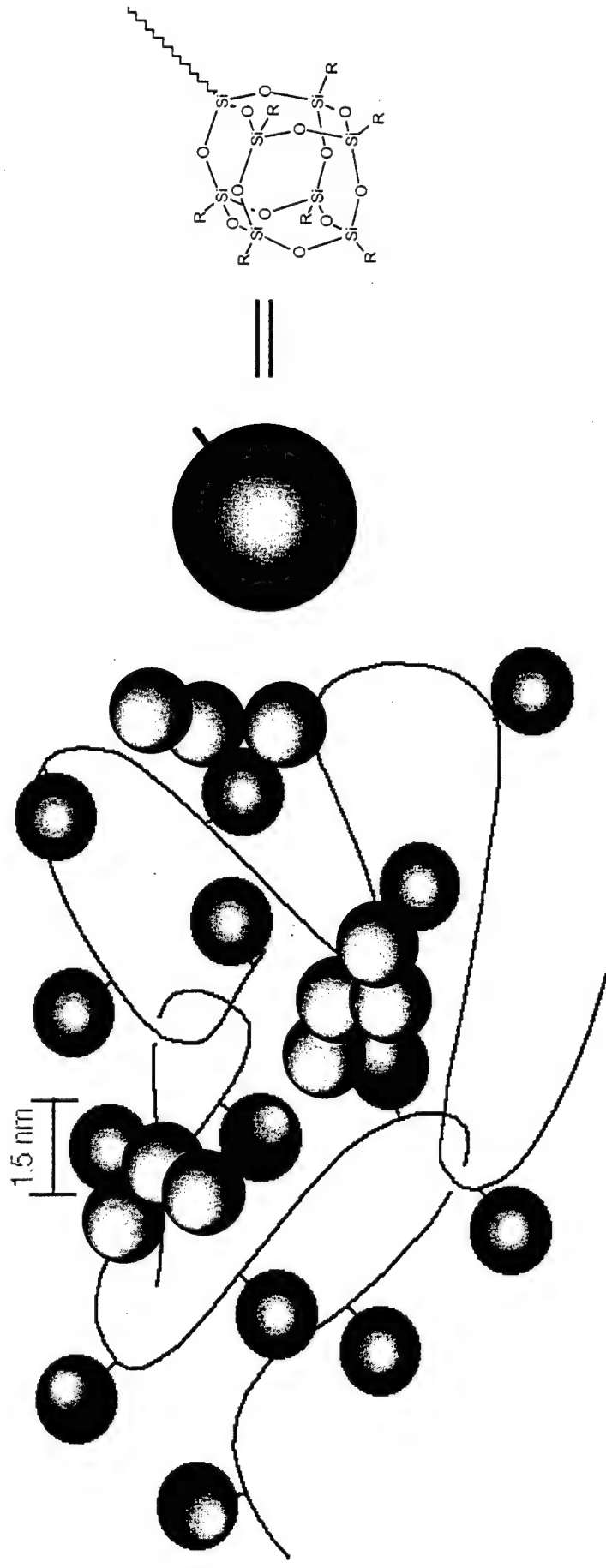
## >100 polymer systems

- POSS-rubber\*
- POSS-urethane\*
- POSS-epoxy\*
- POSS-phenolic\*
- POSS-imide\*
- POSS-teflon

monomers and polymers.

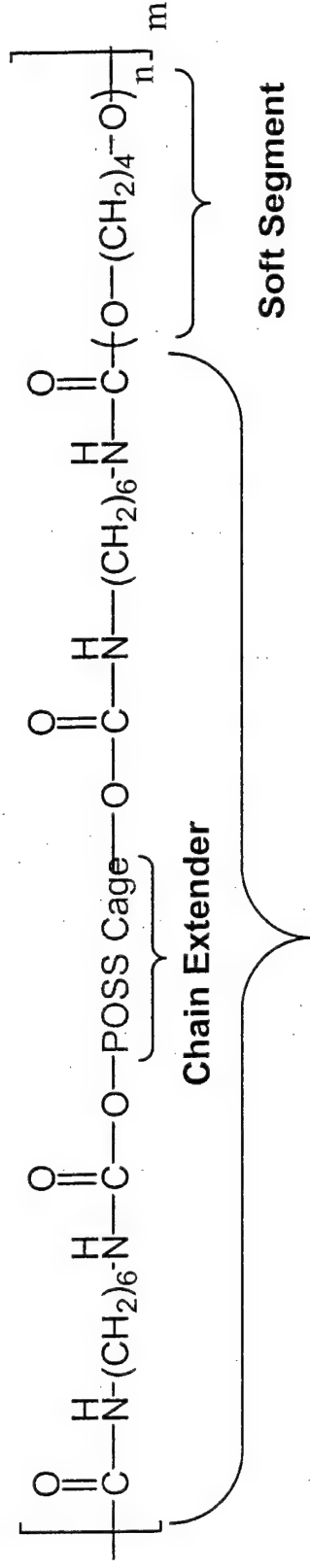
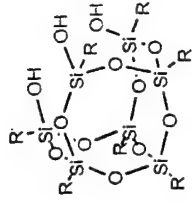
***“POSS-technology is sustainable  
via dual-use markets”***

# Conceptual Model for POSS Polymers



**POSS-POSS interactions?**  
**Entanglement?**  
**Aggregation?**

# POSS-polyurethane Properties



## POSS-polymer improvements

Up to 300 °C increase in the melt transition temperature (rheology studies show the transition from an oil to a true thermoplastic elastomer)

Up to a 100 °C increase in  $T_{dec}$  (29 wt% POSS, still TPE)

Up to 10X increase in moduli (>400% elongation with no destruction of hard segments))

17% POSS incorporation ----> 3X increase in Hardness (Shore A)

*Prof. Andre Lee - Michigan State University*

	Dow data	Neat <i>i</i> -PP (processed)	<i>i</i> -PP blended 2 wt% Methyl <sub>8</sub> T <sub>8</sub>	<i>i</i> -PP blended 5 wt% Methyl <sub>8</sub> T <sub>8</sub>	<i>i</i> -PP blended 10 wt% Methyl <sub>8</sub> T <sub>8</sub>
Tensile Strength @ Yield; ASTM D638	5000 psi (34.5 MPa)	4800 psi (33.0 MPa)	5000 psi (34.5 MPa)	5100 psi (35.1 MPa)	5200 psi (35.8 MPa)
Flexural Modulus (0.05 in/min, 1% secant); ASTM D790A	240,000 psi (1.655 GPa)	235,000 psi (1.620 GPa)	251,000 psi (1.730 GPa)	255,000 psi (1.757 GPa)	262,000 psi (1.80 GPa)
HDT @ 66 psi, as injected; ASTM D648	210 °F (99 °C)	210 °F (99 °C)	221 °F (105 °C)	239 °F (115 °C)	255 °F (124 °C)
Impact Izod @25C ASTM D256A	0.5 ft-lb/in	0.55 ft-lb/in	0.55 ft-lb/in	0.62 ft-lb/in	0.75 ft-lb/in

- The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.

# Key Roadblocks for POSS Materials, Sept. 1998

- Time for Production of POSS feedstocks
- Cost of POSS feedstocks/monomers/polymers
- Volume of POSS feedstocks/monomers
- Structure/Property Relationships
- Blends & Processing

# POSS™ Commercialization and Cost Reduction Campaigns

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In October 1998 Hybrid Plastics and the Air Force Research Laboratory entered into a Cooperative Research and Development Agreement (CRADA) for the commercialization of POSS™ Nanotechnology.

## **Technical Objective:**

- Commercialization of POSS™ Technology.

Also in October 1998 Hybrid Plastics was awarded a 3-year, \$2 million grant by NIST's Advanced Technology Program (ATP) to reduce the cost of POSS Nanostructured™ Chemical Technology by a factor of 100.

## **Technical Objective:**

- Reduce costs of POSS™ Technology from \$1000-\$5000/lb to \$10-50/lb.



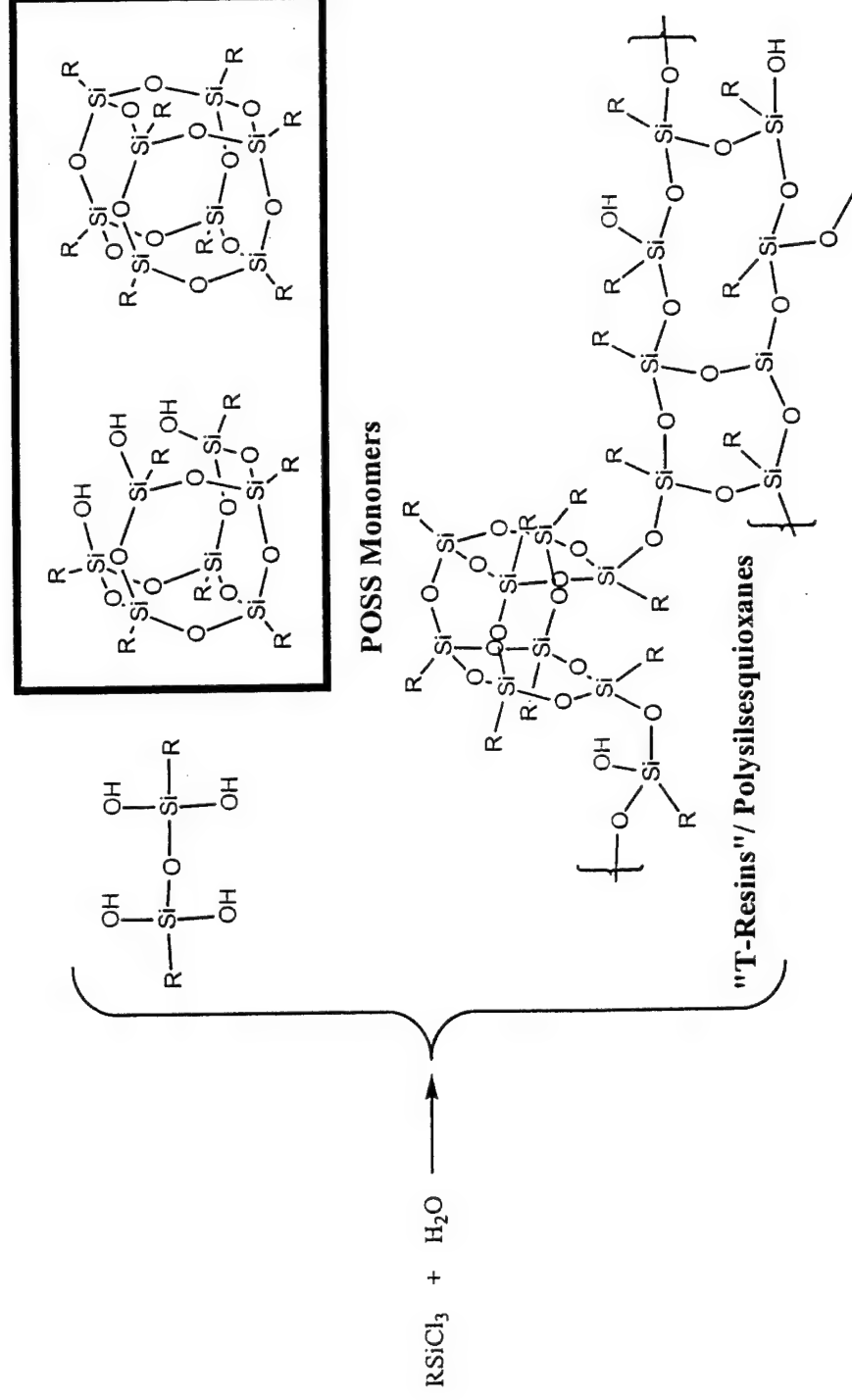
# POSS™ Commercialization and Cost Reduction Campaign

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## Technical Challenges:

- Develop processes for the synthesis of nanostructures from low cost feedstocks.
- Increase efficiency of processes:
  - Increase concentration at least 5 fold.
  - Increase yield to >95%.
  - Increase selectivity for desired products.
- Decrease reaction times from days to hours.
- Develop processes suitable for large scale (kilo-ton) production.
- Develop technology portfolio which will allow:
  - Selective manipulation SiO framework.
  - Control of stereochemistry.
  - Control of functionality.
  - Type of reactive functionality.
  - Degree of reactive functionality

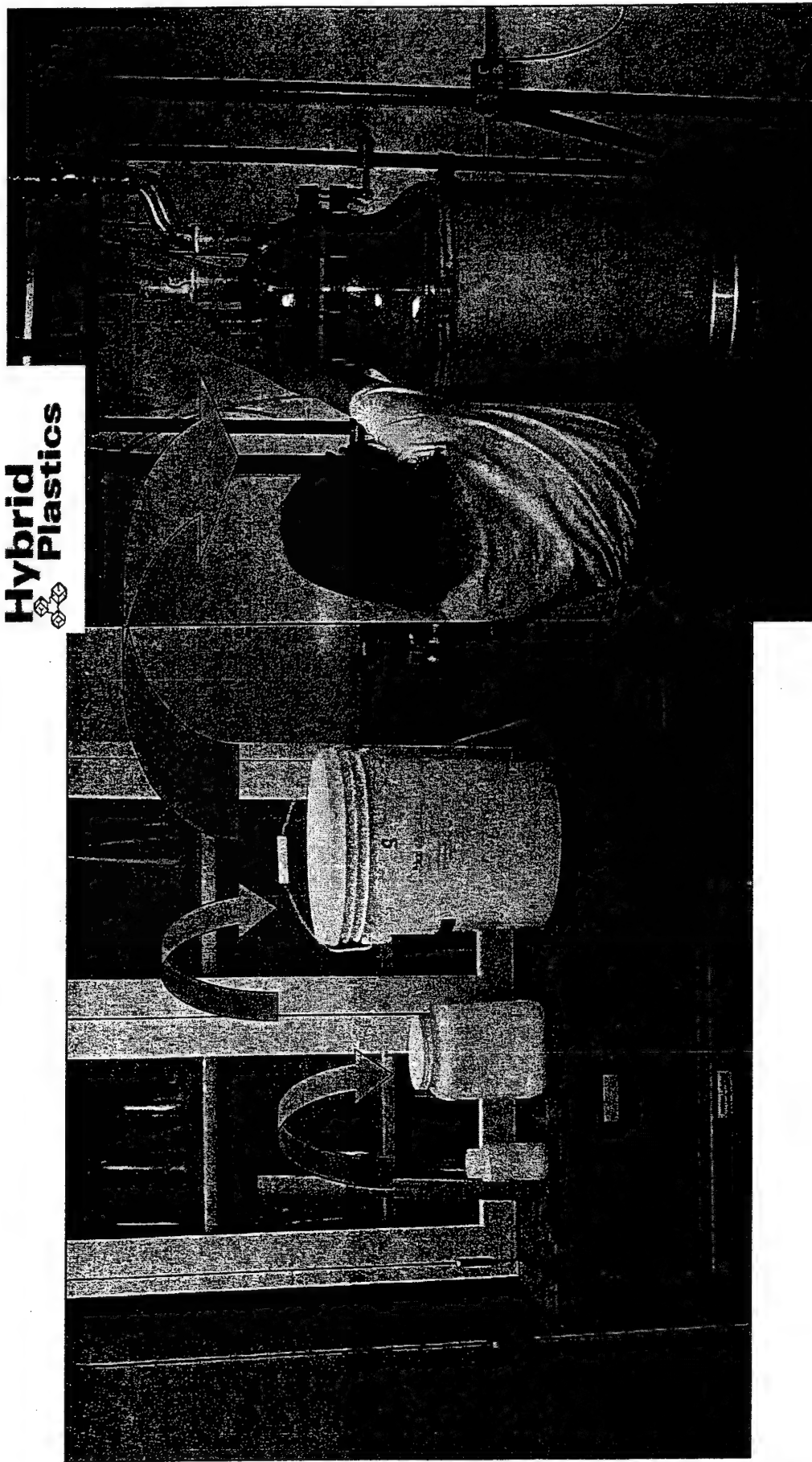
# Volume Increase, Price Reduction



- Traditional silsesquioxane chemistry focused on "T-Resins"
  - Hybrid Plastic's new proprietary routes have resulted in high yields, selectivity, increased [ ]s, and lower cost starting materials
- ↑ ?

**Technology Transfer = Scalability = Price Reduction, Sustainability**

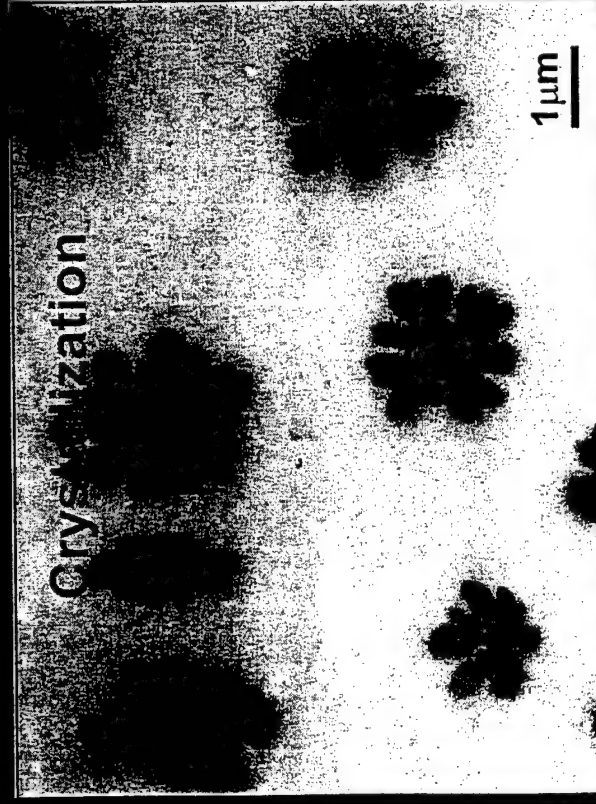
**Hybrid  
Plastics**



**Plant**

Time	1991	1994	1998	2000
Quantity	< 50g	2-5 lb	20-40 lb	> 400 lb
Price	???	\$1000-5000/lb	\$1000-5000/lb	\$20-250/lb

## 6.1 NWV: Processing/Blending



Nanodispersion!!



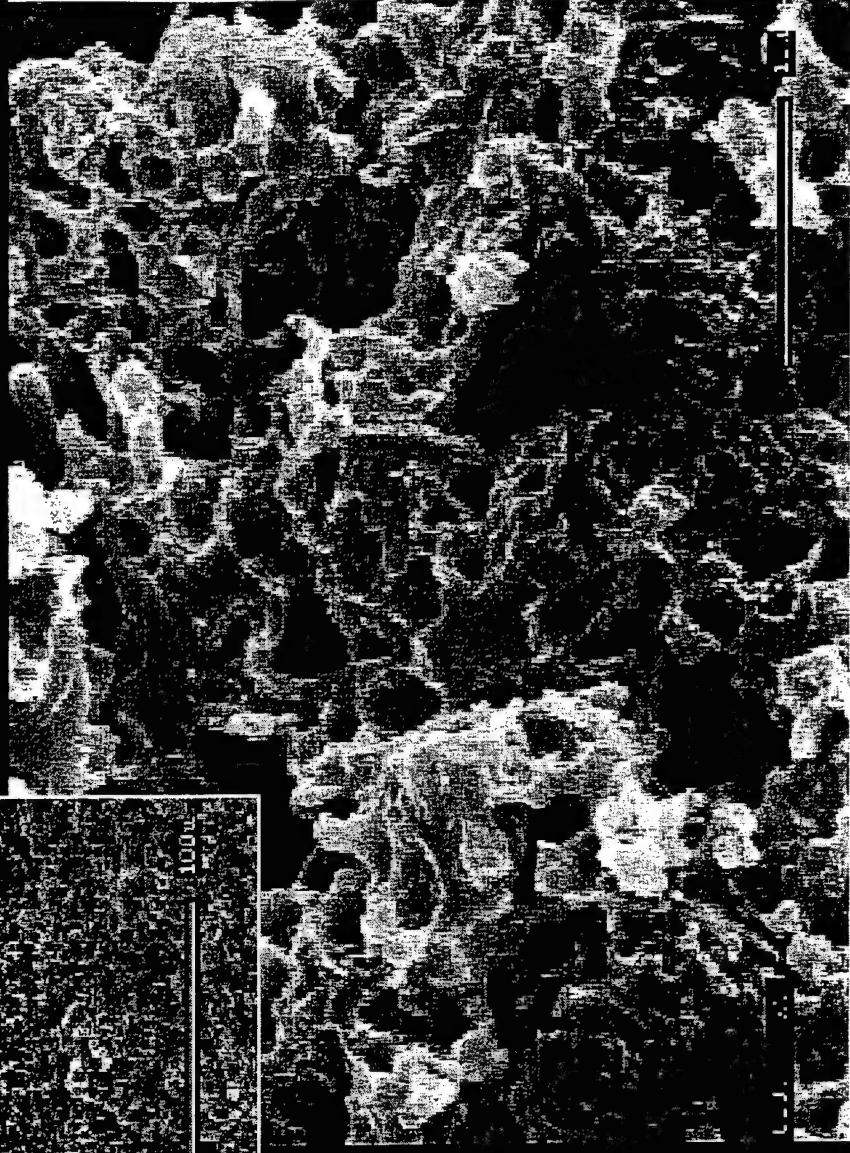
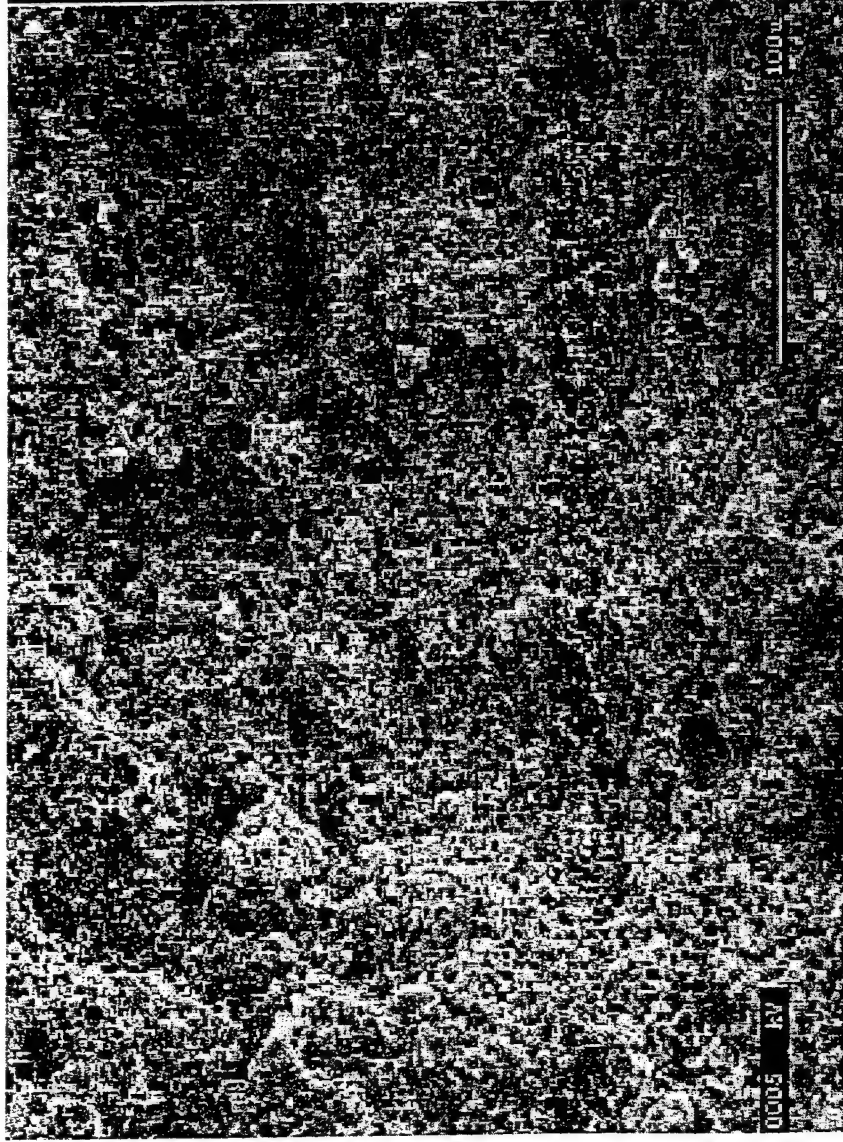
1 μm

**Tech Challenge:** Insolubility of POSS monomers in polymer matrices  
**Success + synthesis of a nanodispersed POSS-Polypropylene (demos)**

**Result:** R&D100 Award in 2000

**R&D**

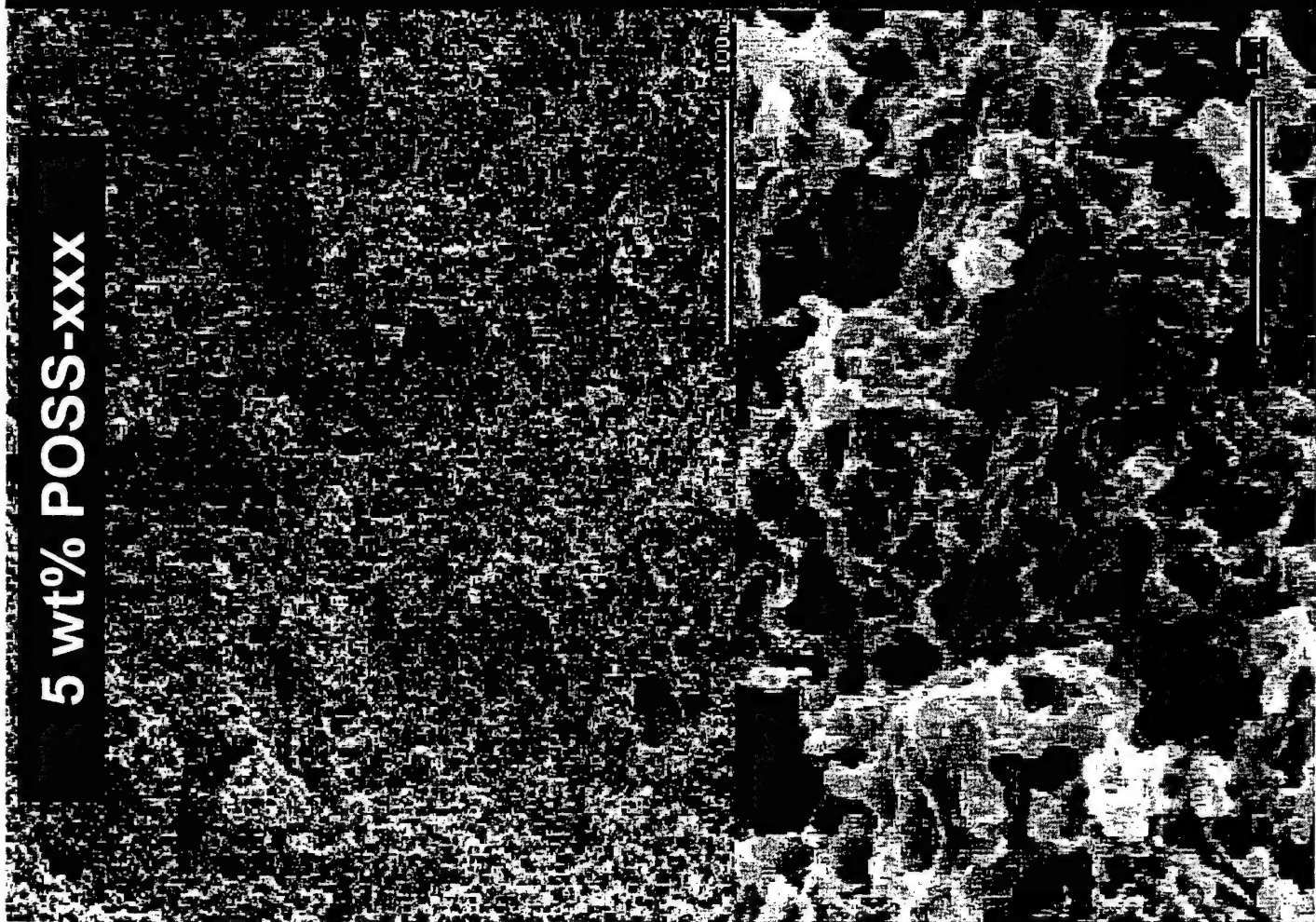
**5 wt% POSS-xxx  
Microfoamed by  
WMR (DUS&T)**



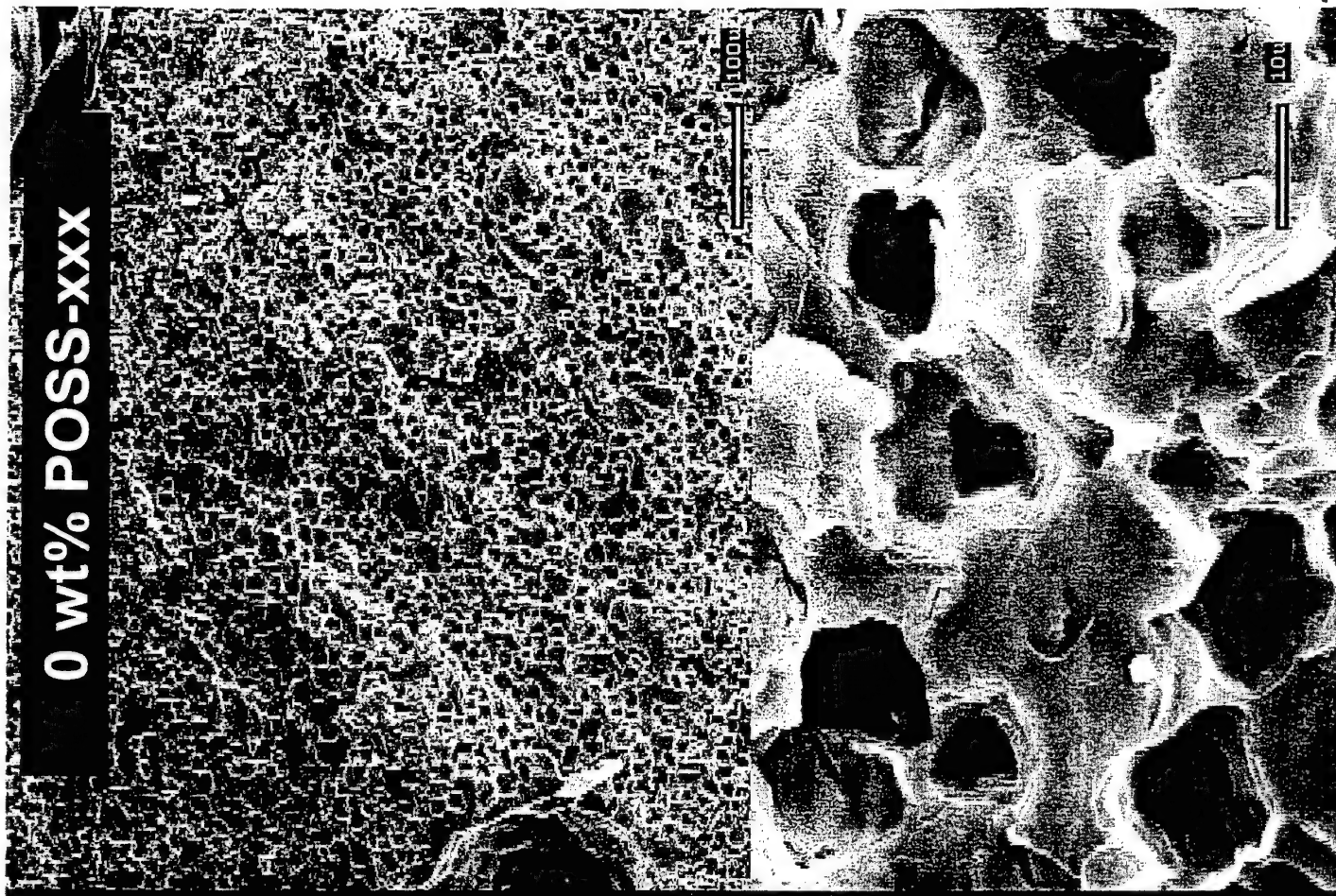
- Fairly uniform foaming
- >25% weight reduction\*
- 33% increase in compression strength & fracture toughness



5 wt% POSS-xxx



0 wt% POSS-xxx



# POSS for fiber coatings

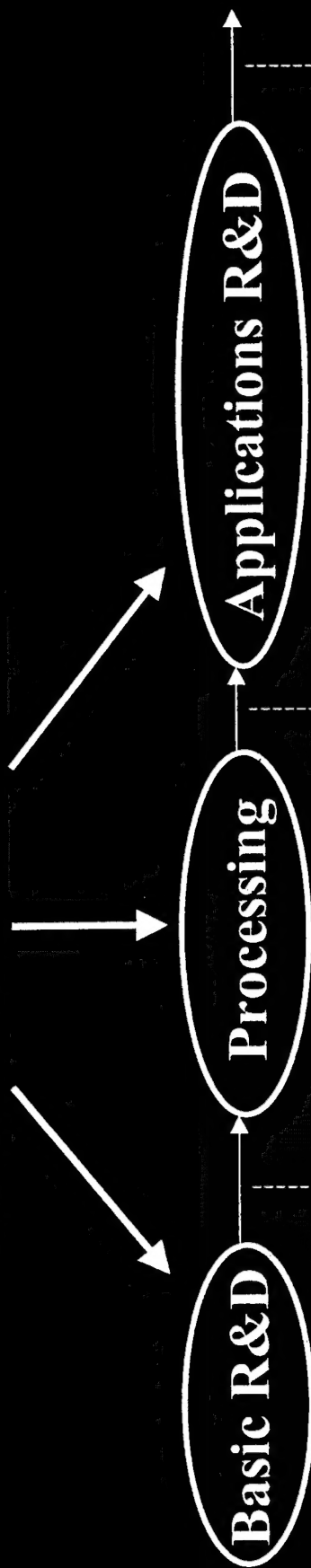


*Uncoated and coated riton fibers*

Successfully developed low-cost, efficient coating process

# Programmatics: Dual Use & Leveraging

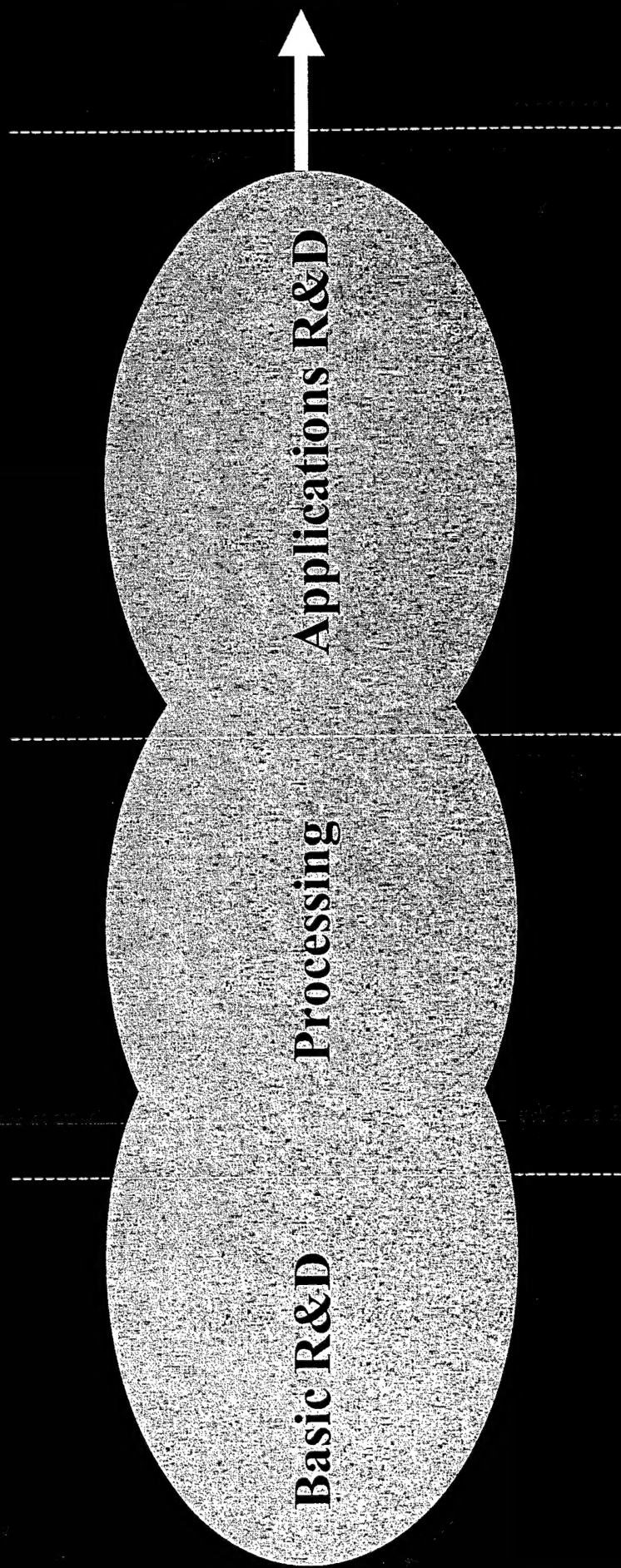
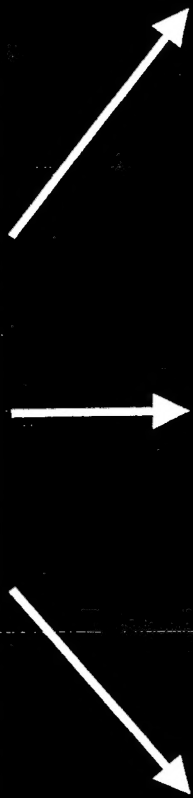
# Polymer Working Group





# Programmatics: Dual Use & Leveraging

## Polymer Working Group



# *CONCLUSIONS*

Academic/Government Lab Collaborations are essential

## Polymer Working Group

Basic R&D goal for controlling/understanding POSS affects on polymer properties is already ahead of schedule (including processing).

Cost, Volume and Production time goals have all been met thanks to Hybrid Plastics & Prof. Frank Feher.

Understanding processing is a key area that is being heavily worked.

POSS applications within government are on critical paths, while industrial interest has increased exponentially with technology transfer in 1998.